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(54) Light-emitting diode

(57) A diode which emits white light when reverse-biased consists of a semiconductor bearing a thick layer of semiconductor oxide (e.g. gallium arsenide oxide and/or alumina). On top of that is a metal (e.g. indium) contact pad. The light appears as a halo around the contact. A second contact on the oxide layer may be used in place of a direct connection to the semiconductor body.

SPECIFICATION

Light-emitting diode

5 This invention relates to a light-emitting diode, and to a method of producing white light.

Light-emitting diodes have been developed which give red or green light, but white light 10 has hitherto been unobtainable.

The present invention is a light-emitting diode comprising a semiconductor bearing a layer of semiconductor oxide, the oxide layer bearing a metal pad, the diode under reverse 15 bias emitting white light. The invention also provides a method of producing white light, comprising reverse-biassing a diode comprising a semiconductor bearing a layer of semiconductor oxide, the oxide layer bearing a 20 metal pad. The light appears as a halo around the edge of the metal pad, and typically is a continuous spectrum over the visible range (wavelengths 420–700nm approximately) and continuing, as might be expected, well into 25 the infra-red.

The semiconductor may be silicon, preferably with an ample superficial trap density, or a III/V semiconductor such as gallium arsenide, which may be bulk grown or epitaxially 30 grown, or a II/VI semiconductor. The gallium arsenide may be p-type or n-type, the latter being preferred. The gallium arsenide has preferred dopant concentration of 10^{16} to 5×10^{17} per ml, but such pre-injected holes 35 are not essential; they do, however, lower the voltage of operation. Excessive doping will eliminate the necessary Schottky barrier.

The oxide layer may be produced as desired, for example by leaving the semiconductor 40 in air, by thermal growth, by depositing a reactive oxide such as Al_2O_3 or silicon nitride or (preferably, for the best reproducibility) by anodising. The oxide layer may be as thin as 10 Å or 20 Å, but in such cases the light-emitting diode might have only a short life. The oxide layer is preferably at least 50 Å 45 thick for reasonable durability, more preferably at least 100 Å thick. For normal conditions, the oxide layer need not exceed 300 Å in thickness, but thicker layers may be advisable for high-temperature operation.

The oxide may be Al_2O_3 or may be a composite oxide, produced for example by plating Al on to GaAs and anodising the 55 whole.

In a transistor having this surface oxide structure, operation would be under forward biasing, not under the reverse bias used for this light-emitting diode. In a transistor operated under reverse bias, the oxide, far from being present to, say, 100 Å or more thickness, would be prevented by all possible means from forming.

The metal, in the case of n-type gallium 60 arsenide, is preferably one with a low work

function. Therefore indium is preferred. Gold will work but is not usually preferred, and aluminium is midway between indium and gold. Gold is preferred in the unusual case

70 where a guard ring is provided around the metal pad to prevent high fields at the perimeter of the pad; under reverse bias, light is then emitted from the whole area of oxide underlying the pad, but is only visible to the 75 extent that it can shine through the metal pad. In that case, the pad is preferably gold, which can be applied in very thin (translucent) layers.

The metal may be evaporated on to the 80 oxide, or applied patternwise by photoresist techniques, or in any suitable way.

If it is desired to make an artefact which is luminescent over an area, rather than punctiformly or linearly, the above guard ring technique is possible but, more preferably, the metal pad would be applied as a grid extending over the desired area.

Using n-type GaAs, doped at 10^{16} /ml, with indium as the metal, light is emitted at a 90 current of 10mA. With p-type GaAs, the current might have to be over 100mA. Although the power consumptions may be similar, the larger current makes the p-type less stable.

The diode may be annealed before use; this 95 will usually change the trap level distribution and hence the spectrum produced. Increasing the voltage increases the brightness but does not alter the spectrum, this being in passing a demonstration that the light emitted is not 100 due to thermal radiation following breakdown of some layer. Nor is the emission due to plasmon excitation, since that requires a rough metal pad surface (such as indium offers), while the present diode will work with 105 aluminium pads, which are smooth.

The temperature range of operation is at least from 77K to 393K for n-type GaAs/GaAs oxide/In, the lower temperatures favouring efficiency.

110 The invention also includes a triode, comprising the diode set forth above, wherein the metal pad has associated with it but spaced from it a second metal pad borne on the oxide layer. The second metal pad may be an annulus surrounding the first metal pad, or the first and second metal pads may be in the form of alternating aligned or criss-crossing (non-contacting) strips.

The second metal pad may be spaced a 120 clear 10^2 to 10^4 Å from the first metal pad. The metals may be the same, which makes for ease of fabrication, or different, such as to induce more holes in the semiconductor. In operation, the second metal pad is raised to a 125 potential positive with respect to the first metal pad. The semiconductor, on its face opposite the metal pads, may be earthed, but need not be if the second and first pads are respectively forward and reverse biased.

130 The smaller the clear spacing between the

pads, the lower the voltage at onset of luminescence, and thus the greater the efficiency. Using n-type GaAs, doped at $10^{16}/\text{ml}$, with a 20 Å layer of oxide, and the pads a clear 5 1000 Å apart, luminescence may be expected at an applied potential of 2V; current consumption might be around 20mA.

Under forward biasing of the second metal pad, positive holes are formed in the n-type 10 GaAs, giving rise at will to an inversion layer, which migrates under the electric field to the first metal pad, at the edge of which the field is strong enough to cause electrons from the reverse-biased first metal pad to annihilate 15 the holes with emission of energies in the visible range. In this way, light is produced without having to rely on avalanching.

The invention also provides a double-oxide light-emitting diode, being layers successively 20 of a metal, alumina, metal-oxide and semiconductor, both the alumina and oxide being from 20 Å to 70 Å thick (thinner than for charge-storage devices). Light intensity may be improved by this structure.

25 The choice of metal for that pad which is to be reverse biased is governed by the requirement that the difference in Fermi levels (volts) between the metal and the semiconductor must be too small to break down the oxide 30 layer. As the oxide layer will withstand voltages in direct proportion to the thickness of the layer, that layer can be made as thick as necessary, at the cost of efficiency. The Fermi level difference between gold and gallium 35 arsenide is about 1.3 volts, which would break down a thin oxide layer. The Fermi level difference between the metal indium and the semiconductor gallium arsenide is very small, making those an ideal pair. Aluminium in this 40 respect is intermediate between indium and gold.

Diodes were made up using n-type GaAs differing in dopant (pre-injected hole) concentration, and differing in choice of metal pad. 45 The diodes required the following approximate reverse biasing to start passing current.

Dopant	Metal	Bias	Current
50 $10^{16}/\text{ml}$	Al	- 19V	5mA
$10^{18}/\text{ml}$	In	- 15V	10mA
$10^{17}/\text{ml}$	Al	- 9V	20mA

55 The above values for 'current' are the approximate currents passed at a given intensity of light emission by each diode. The structure with the lowest voltage of operation is thus 60 not necessarily the most efficient.

An exemplary light-emitting diode was constructed as follows:

A sample of n-type gallium arsenide (hole density $10^{16}/\text{ml}$) was etched in a solvent 65 containing 2 weight percent NaOH and 4

volume percent H_2O_2 —which at room temperature dissolves gallium arsenide at about 1000 Å/minute.

The sample was anodised as described in 70 British Patent Specification 1503411, to give a native oxide thickness of 100 Å. A spot of indium was evaporated on to the oxide, and a pin was rested on the spot. The sample was resting on a conductive grid. A bias of - 15V 75 was applied between the pin and the conductive grid. A current of 10mA flowed, and white light was emitted around the edge of the spot.

80 CLAIMS

1. A light-emitting diode comprising a semiconductor bearing a layer of semiconductor oxide, the oxide layer bearing a metal pad, the diode being such as to emit white light 85 when reverse-biased.
2. A light-emitting diode according to Claim 1, wherein the semiconductor is silicon having a substantial superficial trap density.
3. A light-emitting diode according to 90 Claim 1, wherein the semiconductor is a III/V or a II/VI semiconductor.
4. A light-emitting diode according to Claim 3, wherein the semiconductor is a gallium arsenide.
- 95 5. A light-emitting diode according to Claim 4, wherein the gallium arsenide is n-type.
6. A light-emitting diode according to any of Claims 2 to 5, wherein the semiconductor 100 has a dopant concentration of 10^{16} to $5 \times 10^{17}/\text{ml}$.
7. A light-emitting diode according to any preceding claim, wherein the layer of semiconductor oxide is at least 50 Å thick.
- 105 8. A light-emitting diode according to Claim 7, wherein the layer of semiconductor oxide is from 100 to 300 Å thick.
9. A light-emitting diode according to any preceding claim, wherein the semiconductor 110 oxide is Al_2O_3 or contains Al_2O_3 .
10. A double-oxide light-emitting diode, comprising a light-emitting diode according to Claim 9 wherein the Al_2O_3 is in the form of a layer interposed between the metal pad and 115 the oxide of the semiconductor, both the Al_2O_3 and the oxide of the semiconductor being from 20 Å to 70 Å thick.
11. A light-emitting diode according to Claim 4 or any claim dependent thereon, 120 wherein the metal pad is of indium.
12. A light-emitting diode according to any preceding claim, wherein the metal pad has the form of a grid extending over that area of the oxide layer which is to emit light.
- 125 13. A light-emitting diode according to any of Claims 1 to 10, wherein the metal pad is of translucently thin gold and further comprising a guard ring around the pad.
14. A light-emitting diode according to 130 Claim 1 and substantially as hereinbefore de-

scribed.

15. A light-emitting triode comprising a light-emitting diode according to any preceding claim further comprising a second metal pad spaced from the (first) metal pad and also in contact with the semiconductor oxide.
- 5 16. A light-emitting triode according to Claim 15, wherein the second metal pad is an annulus surrounding the first metal pad.
- 10 17. A light-emitting triode according to Claim 15, wherein the first and second metal pads are in the form of alternating aligned or criss-crossing (non-contacting) strips.
18. A method of producing white light, comprising reverse-biassing a diode or triode according to any preceding claim.
- 15 19. A method according to Claim 18, wherein the reverse-biassing is arranged to produce a current flow of at least 10mA.

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